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(54) **A composition of restorative material.**

(57) A composition of restorative material, especially useful as a dental filling material, comprising finely divided inorganic filler material and polymerizable monomer components is disclosed. Said composition contains (A) from about 50 to about 95% by weight of finely divided, inorganic filler material which is safe and effective for use in a dental filling in the human body, wherein at least 50% by weight of said filler material is at least one nitride substance having a Moh's hardness of at least 7 and is selected from the group consisting of vanadium nitride, boron nitride, aluminum nitride, silicon nitride, titanium nitride and zirconium nitride, and (B) from about 50 to about 5% by weight of polymerizable monomer component capable of polymerizing to form a binder resin for dental filling materials.

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A composition of restorative material

The present invention relates to a composition of restorative material, which is especially suitable for medical or dental use.

Among the materials for medical or dental use, and for dental use, in particular, the dental amalgam consisting of silver alloy and mercury, and silicate cement have hitherto been used as restorative filling material. The amalgam, however, shows a low degree of marginary seal because of inferior impact strength in addition to interferior bonding property to tooth, entailing the fear of exerting unfavourable influences on the human body in the point of toxicity. Further the silicate cement is readily soluble and entails such shortcomings as to be great in pulpal irritation in addition to a low degree of bonding property to tooth and inferior marginary seal.

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Whereupon, for anterior teeth developments have been made of material consisting predominantly of bisphenol A diglycidyl methacrylate (hereinafter called "Bis-GMA" for short) and inorganic filler, such as α-quartz (hereinafter called the Bis-GMA type composite resin), as new restorative filling material substituting for conventional silicate cement (refer, for instance, to the United States Patents 3,539,533; 3,066,112; 3,926,906, etc.), which has been improved in such properties as compressive strength, water resistance, pulpal irritation and so on as compared to conventional material, such as said silicate cement, and widely used, but it is still far from satisfactory in the aspect of physical properties, such as hardness, compressive strength, abrasion resistance and so on, or bonding to tooth and the like. In the case of Bis-GMA it is in such a condition even in anterior tooth, not to mention that it is next to impossible to apply to molar which is more high in occlusal pressure than anterior tooth.

With the Bis-GMA type composite resin, for reason that said physical functions are not enough it can be said that Bis-GMA is insufficient in physical properties as resin, being low in cross-link and that high viscosity of Bis-GMA, even if diluents were jointly used, restricts the amount of the inorganic filler which is jointly used with the purpose of improving physical properties of restorative filling material.

For reason that the Bis-GMA type composite resin is scarce in the bonding property to tooth it

can be mentioned that because of joint use of a great deal of inorganic filler in addition to somewhat scarce bondability to tooth of Bis-GMA enhances the viscosity of the composite resin resulting in no good wettability on the tooth surface.

In order to improve various such shortcomings with the Bis-GMA type composite resin attempts were made to enhance the cross-link of the resin and increase the amount of inorganic filler in joint use by using such low viscosity multifunctional monomers as trimethylolpropane trimethacrylate (hereinafter called "TMPT" for short) instead of Bis-GMA as disclosed in British Patent No. 1,451,262, for instance, but in the case of TMPT bonding to tooth is hardly shown because of its having no polar groups and viscosity of TMPT is too low, which gives rise to such problems as lacking in the surface curability as the composite resin and settling of inorganic filler in paste condition.

In the case, further, of TMPT, pulpal irritation by the residual monomer is very severe.

The instant inventors studied with the purpose of solving various said drawbacks with conventional dental material, in consequence of which it was found that by using resin-forming material consisting predominantly of the hereinafter-described acrylic monomer of the specified structure there could be obtained material for medical or dental use excellent in various physical properties, such as hardness, compressive strength, abrasion resistance and so on, weak in tissue irritation and in addition, excellent in bonding to the hard tissue of the human body.

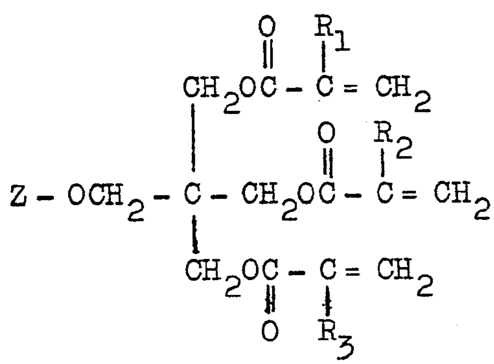
The present invention is designed to provide resin-forming material suitable for medical or dental use which is excellent in various physical properties, such as hardness, compressive strength, abrasion resistance and so on, weak in the tissue irritation and added to this, extremely good in the bonding to the

hard tissue of the human body.

Another purpose of the present invention is to provide resin-forming material suitable for medical or dental use which is excellent in various said physical properties, tissue irritation and bonding to the hard tissue and good in operation in its practical use.

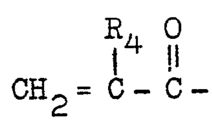
The other purposes and merits of the said resin-forming material of the present invention will be clear from explanations which follow.

According to the present invention, the said purposes and merits could be achieved by resin-forming material suitable for medical or dental use comprising at least one member of compound represented by the following formula (I):



..... (I)

wherein Z stands for a hydrogen atom or a group represented by the following formula

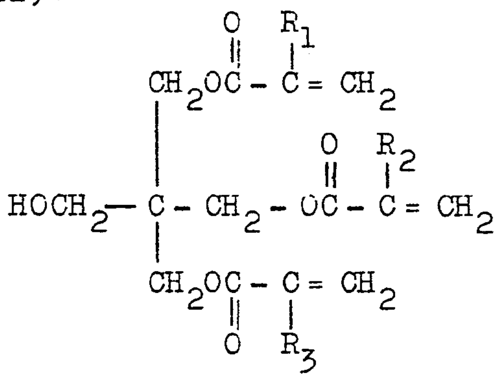


and

R_1, R_2, R_3 and R_4 may be each identical or different and stand for a hydrogen atom, methyl group, ethyl group or n- or iso-propyl group.

Compounds represented by the said formula (I) divide broadly into two classes, one is compounds represented by the following formula (II) and the other is compounds represented by the following formula (III).

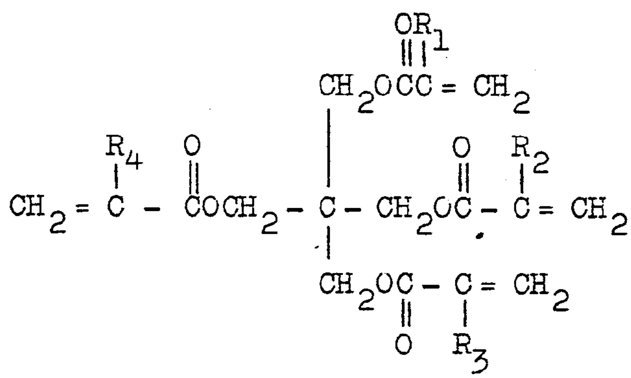
Formula (II):



.... (II)

wherein R_1, R_2 and R_3 are as defined in the formula (I).

Formula (III):



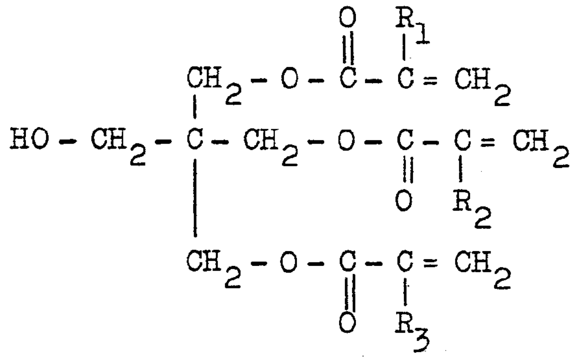
.... (III)

wherein R_1, R_2, R_3 and R_4 are as defined in the formula (I).

According to the present invention at least one member of compound represented by the formula (II) or (III) can be used as resin-forming material suitable for medical or dental use.

In the present invention it is preferred to use, as medical or dental resin-forming material, compositions comprising

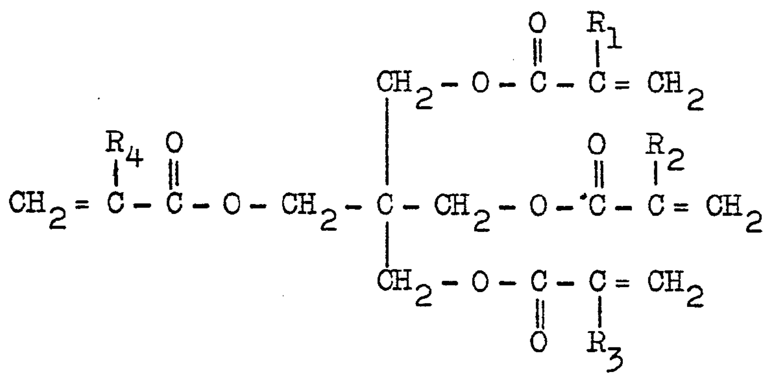
(1) 30 - 100% by weight of at least one member of compound represented by the following formula (II):



.... (II)

wherein R_1, R_2 and R_3 are as defined in the formula (I) and

(2) 0 - 70% by weight of at least one member of compound represented by the following formula (III):



.... (III)

wherein R_1, R_2, R_3 and R_4 are as defined in the formula (I).

With the resin-forming material of the present invention the compound represented by the formula (II) should advantageously be mixed in proportions of preferably 30 - 95% by weight, more preferably 40 - 80% by weight and most preferably 45 - 70% by weight and the compound represented by the formula (III) in proportions of preferably 5 - 70% by weight, more preferably 20 - 60% by weight and most preferably 30 - 55% by weight. Reasons: If the compound represented by the formula (II) is less than 30% by weight, viz., the compound represented by the formula (III) is in excess of 70% by weight, in the case, in particular, of using as dental filling material or restoratives for crown bridge, it tends

to deteriorate in the bonding to tooth and operation.

In the instant invention the said formulae (I), (II) and (III) wherein R_1, R_2, R_3 and R_4 are hydrogen or methyl, in particular, are preferred. In this case, most typically the respective R_1, R_2 and R_3 in the formula (II) or the respective R_1, R_2, R_3 and R_4 in the formula (III) represent hydrogen or methyl. Not only that, but those in which part of R_1, R_2, R_3 and R_4 represents hydrogen, whereas another part of them represents methyl, viz., mixed esters of acrylic acid and methacrylic acid, are also preferred.

As typical examples of compounds represented by the formula (II) are cited tetramethylolmethane triacrylate and tetramethylolmethane trimethacrylate, for instance. As typical examples of compounds represented by the formula (III) are cited tetramethylolmethane tetraacrylate and tetramethylolmethane tetramethacrylate, for instance.

Conventionally, as already mentioned, it is known to use triacrylate or trimethacrylate esters of trimethylolpropane, but the compound of the said formula (II) used in the present invention is characterized by possessing another methylol group ($-CH_2OH$) besides the triacrylate or trimethacrylate esters and the compound of the said formula (III) is characterized in that it is a tetrafunctional acrylate or methacrylate ester.

The compound of the said formula (II) is excellent in bonding to the hard tissue of the human body by the effect with the methylol group and by using such compound of the formula (II) and compound of the formula (III) in combination, in particular, resin for medical or dental use can be advantageously formed which is excellent in bonding to the hard tissue of the human body as well as in the compressive strength.

In the case, further, of using a combination of the compound of formula (II) and the compound of

formula (III), the composite resin formed therefrom is extremely excellent in water resistance besides the said characteristics and shows very excellent operation on the occasion of its practical use.

On top of that, the compounds of the present invention represented by the formulae (II) and (III) can be used in combination with other polymerizable monomers, such as conventionally known resin-forming monomers for medical or dental use. In this case, the amount in which the other monomers are incorporated should preferably be set at 40% by weight or less, more preferably 30% by weight or less and most preferably 20% by weight or less. In the case where monomers other than those of formulae (II) and (III) are contained in as great an amount as to exceed 50% by weight, there is the fear of causing the lowering of various excellent characteristics of the resin composition of the present invention as the above and it is not preferred. In this connection, as typical examples of the polymerizable monomers referred to here can be cited bismethacryloxyethoxydiphenylpropane, Bis-GMA, bisphenol A dimethacrylate, neopentylglycol dimethacrylate and so forth.

The resin-forming material of the present invention, in its practical use, should usually be used as a composition in admixture of a catalyst for causing the polymerization of the compound of the formula (II) and/or compound of the formula (III) and an activator for accelerating the formation of free radicals by the reaction with such a catalyst.

Furthermore, the compounds of the formula (II) and/or formula (III) can be used in combination with any inorganic fillers for medical or dental use being non-noxious to the human body with great hardness, such as powdered quartz, powdered glass, glass beads, powdered aluminum oxide, borosilicate glass, barium glass, hydroxy apatite and alumino silicate, in addition to the catalyst

and activator. These inorganic fillers, although it differs according to use, should preferably have Mohs' scale of hardness of at least 5 and at least 6, in particular. In this case, however, physical properties as material for medical or dental use go much better if it is used in combination with the hereinafter-described specified metal nitride discovered anew by the instant inventors. The said inorganic filler should preferably account for 50 - 95% by weight, preferably 50 - 90% by weight, and most preferably 70 - 90% by weight, based on the total amount with the resin-forming compound (monomer) such as compound of the formula (II) or (III).

If the inorganic filler is to be pretreated with a keying agent, such as γ-methacryloxypropyltrimethoxysilane, vinyltriethoxysilane and so forth, the bond between the formed resin and the inorganic filler will be intensified and physical properties as material for medical or dental use will be further improved.

The monomer of the present invention represented by the said formula (II) or (III) is readily polymerized and cured by means of catalyst. On this occasion, the application of heat often does harm to the human body when using in fields associated with the human body and it is preferred to divide the said monomer, into two, a two liquid form, one containing a catalyst and the other containing an activator, in such a manner as to be able to cure the monomer at normal temperature when used and mix the both immediately prior to use.

As the catalyst peroxide is preferred and it should preferably be used in combination with the activator. As the peroxide catalyst can be cited, for instance, diacyl peroxides, such as benzoyl peroxide, parachlorobenzoyl peroxide, 2,4-dichlorobenzoyl peroxide, acetyl peroxide, lauroyl peroxide

and so on, hydroperoxides, such as tertiary butyl hydroperoxide, cumene hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide and so on, ketone peroxides, such as methyl ethyl ketone peroxide and so on, peroxycarbonates, such as tertiary butyl peroxybenzoate and so on, etc.

These peroxide catalysts should preferably be used in proportions of 0.1 - 2.5% by weight based on the total weight of the polymerizable monomers of the present invention represented by the said formula (II) or (III).

As the activator capable of use in combination with the peroxide can be cited, for instance, tertiary amines, such as N,N-bis-(2-hydroxyethyl)-4-methylaniline, N,N-bis-(2-hydroxyethyl)-3,4-dimethylaniline, N,N-bis-(2-hydroxyethyl)-3,5-dimethylaniline, N-methyl-N-(2-hydroxyethyl)-4-methylaniline, 4-methylaniline, N,N-dimethyl-p-toluidine, N,N-dimethylaniline, triethanolamine and so on, and in addition, transition metal ions, such as cobalt naphthenate, cobalt octanate and so on, amine salts of p-toluenesulphonic acids and sulphinic acids and so forth.

These activators can generally be used in proportions of 0.1 to 2.5% by weight based on the total weight of the said polymerizable monomers.

The monomer of the present invention can also be polymerized and cured by irradiation of ultraviolet rays. In this case, it is not necessary to formulate into the said two-liquid form and it is preferred to use a photosensitizer in the amount of 0.1 - 10% by weight based on the total weight of the polymerizable monomers. As the photosensitizer can be cited, for instance, carbonyl compounds, such as benzoin, benzoin methyl ether, benzoin ethyl ether, acetoin, benzophenone, p-chlorobenzophenone, p-methoxybenzophenone and so on, sulphur compounds, such as tetramethylthiuranium monosulphide, tetramethylthiuranium disulphide and so on,

azo compounds, such as azobisisobutyronitrile, azobis-2,4-dimethylvaleronitrile and so on, peroxide compounds, such as benzoyl peroxide, tertiary butyl peroxide and so on, etc.

For the enhancement of preservability of the resin composition it is effective to add an UV absorber such as benzophenone type compound, such as 2-hydroxy-4-methylbenzophenone, in the amount of 0.5 - 2.0 parts by weight based on 100 parts by weight of the resin composition, or a stabilizer generally called a free radical inhibitor, such as p-methoxyphenol, 2,5-di-tert.butyl-4-methylphenol and so on, in the amount of 0.05 - 0.20 part by weight based on 100 parts by weight of the resin composition.

For a method of using such resin compositions, it is very convenient to prepare in advance a paste-like substance (paste A) comprising an inorganic filler, resin composition and activator and a paste-like substance (paste B) comprising an inorganic filler, resin composition and catalyst, for instance, since the polymerization is initiated upon mixing these two pastes when used by doctors.

In the case of using such material in restoration of the hard tissue of the human body, such as teeth and bones, the said material possesses as such sufficient bonding to the hard tissue, but it is also effective to apply the said material after precoating the hard tissue with the bonding agent in ordinary use, such as 2-hydroxyethylmethacrylate and so on, with the purpose of improving the bonding to the hard tissue. As the said bonding agent, the subject matter of another co-pending Patent Application filed claiming the priority based on Japanese Patent Application No. 54-44751, discovered anew by the instant inventors, can be very effectively used in the point of bondability which consists predominantly of a composition comprising 50 - 99.5% by weight of polymerizable acrylate esters

and/or methacrylate esters having hydrophilic groups comprising carboxyl, epoxy, amino or hydroxyl and 0.5 - 50% by weight of at least one member of organic metal compound selected from the group consisting of alkoxyl-containing titanium compounds and silicon compounds.

Thus, according to the present invention there can be obtained resin compositions suitable for medical or dental use which are extremely excellent in various physical properties after curing, such as hardness, compressive strength, abrasion resistance, weak in tissue irritation and good in bonding to the hard tissue of the human body and on top of that, excellent in operation in practical use.

Further, the resin-forming material of the present invention can be advantageously used as in medical or dental use not only as material for bone cement and artificial bone in the orthopedic surgery and restorative surgery field but also as restorative material for crown bridge, core material for crown, dental cement, filling material, cavity lining material, root canal filling material and so on, in the operative dentistry and prosthetic dentistry field in particular.

[Implant material suitable for medical or dental use]

In the next place, explanations will be given of implant material of the present invention for medical or dental use, viz., for the human body.

As typical examples of composite resin-forming material obtained from a combination of conventional resin-forming material and inorganic filler can be cited, for instance, bone cement and artificial bone material in the orthopedic surgery and restorative surgery field or restorative material for crown bridge, core material for crown, dental cement, filling material, cavity lining material, root canal filling material and so forth in the operative dentistry and prosthetic

dentistry field.

This composite resin for medical or dental use has excellent functions as compared to direct filling resin and inorganic cements conventionally used in the above fields in the points of bonding, water resistance, compressive strength, abrasion resistance and impact resistance, in particular.

In the case of curing by applying the conventional composite resin-forming material for dental use to molar in the operative dentistry and prosthetic dentistry field, for instance, clinical examples show that the form is lost in a short period of time because of markedly high occlusal pressure and frictional force in the molar and that it is difficult to use it stably over a long period of time and in order to make it applicable to molar there is demanded the advent of composite resin for dental use having more high mechanical strengths, such as compressive strength, abrasion resistance, impact resistant function and so on. Conventionally, metal material and dental amalgam are mainly used in the molar, but the metal material presents a problem in the point of convenience, whereas the dental amalgam, on the other hand, leaves a problem to solve in the point of toxicity and of recurrent caries caused from the property inherent in the amalgam and it is not satisfactory material.

The composite resin suitable for medical or dental use is usually made up of a mixture of resin-forming material and various powdery fillers, such as powdered quartz filler, powdered borosilicate glass filler and so on, but affected, in particular, by a low degree of hardness and abrasion resistant function these powdery fillers possess, the composite resin obtained was not of high mechanical strength and high abrasion resistance, in particular, required of it in the practical aspect no matter what resin-forming material might be used.

Of conventionally known fillers, however, powdered alumina filler shows exceptionally high hardness and abrasion resistance. Alumina is a material excellent in abrasion resistance, having Mohs' hardness of 9, but because of no good bonding to the resin for medical or dental use, satisfactory resin-forming material for medical or dental use cannot be obtained even if it underwent various surface treatments.

The instant inventors found that the specified metal nitride, as compared to various conventional powdered fillers, should have a higher degree of hardness and abrasion resistance and better bonding to the resin for medical or dental use and accordingly, should have much higher mechanical strengths, such as compressive strength, abrasion resistance or impact resistance, when using as the composite resin-forming material.

The present invention is designed to provide implant material suitable for medical or dental use, composite resin-forming material containing such implant material (or filler) with extremely high mechanical strengths applicable to all medical fields, such as orthopedic surgery and restorative surgery field or operative dentistry and prosthetic dentistry field and so on.

According to the present invention, the said purposes and merits could be achieved by the restorative implant material of the human body characterized by comprising nitride of at least one member of metal selected from the group consisting of Group IVB, Group VB and Group VIB in the Periodic Table of elements and boron, aluminum and silicon and having Mohs' hardness of at least 7.

The said metal nitride may contain nitride of metal other than the said metals, such as nickel, cobalt and manganese, provided that it remains to be of as small an amount as about 10% or less, and 5% or less, in particular, based on the amount of the said metal

nitride. Even in such cases, it is necessary for the nitride to have overall Mohs' hardness of at least 7 and preferably at least 9.

The metal forming the nitride of the present invention is at least one member of metal selected from the group consisting of titanium, zirconium, hafnium (the foregoing belong to Group IVB of the Periodic Table), vanadium, niobium, tantalum (the foregoing belong to Group VB of the Periodic Table), chromium, molybdenum, tungsten (the foregoing belong to Group VIB of the Periodic Table), boron, aluminum and silicon.

Of the said metal nitrides, particularly preferred in the present invention is nitride of at least one member of metal selected from the group consisting of vanadium, boron, aluminum and silicon. Nitride of silicon, in particular, is preferred since it is high in hardness, great in bondability to the resin-forming material and its cured resin and economically low in costs.

The said metal nitride of the present invention should advantageously have Mohs' hardness of at least 9, in particular.

The said metal nitride, the implant material of the present invention, may be used in any form, such as rod, pellet, powder and so on, but it is preferred to use as composite resin-forming material by mixing in powder form, in particular, to the optional one of resin-forming materials (monomers) for medical or dental use being conventionally known as aforesaid or belonging to the present invention.

The said metal nitride of the present invention can fully exhibit effect even if used in combination with materials applicable to the orthopedic surgery and restorative surgery field or operative dentistry and prosthetic dentistry field other than the resin-forming material, such as conventionally known zinc phosphate cement, and silicate cement.

The restorative implant material for the human body of the present invention should preferably be in powder form, in particular, and its particle diameter should preferably fall in the range of 50 microns or less and 0.1 - 50 microns, in particular. If the particle size is less than 0.1 micron, in some cases, the paste comprising the composite resin-forming material in uncured condition may overly increase in viscosity. If it is in excess of 50 microns, on the contrary, the resin and filler tend to readily separate from each other after mixed together. In some cases, it is practically rendered difficult to operate. The implant material material of the present invention should have Mohs' hardness of 7 or more, but preferably it should have Mohs' hardness of 9 or more. If the hardness is less than 7, the purpose of the present invention cannot be achieved in the aspect of physical properties obtained when using as composite substance mixed to the resin. In this connection, of implant material of the present invention, as those which have Mohs' hardness of 9 or more can be cited BN, Si_3N_4 and VN. Further, aluminum nitride is somewhat lower in Mohs' hardness than the said nitrides, but those with Mohs' hardness of about 8 can be obtained with relative ease and hence, aluminum nitride is preferable.

In the case, in particular, of using as restorative material for crown bridge or filling material in molar tooth in the operative dentistry and prosthetic dentistry field, particularly high compressive strength and abrasion resistance are required since it must withstand high occlusal pressure. In this case, therefore, implant material should preferably have Mohs' hardness of 9 or more. In the case, further, of using the implant material of the present invention as filler for medical or dental use, in particular, it should advantageously be precoated with a keying agent prior to use. As such a keying agent any known ones are

available, but a silicon-containing keying agent is particularly preferred. As such a silicon-containing keying agent are particularly preferred silicon-containing organic compounds possessing at least three alkoxy groups, inter-alia, silicon-containing organic compounds possessing at least three alkoxy groups and one organic group containing, as terminal group, a mono-olefinic hydrocarbon residue, primary amino group or epoxy group. As the typical of such preferred keying agents can be cited α-methacryloxypropyltrimethoxysilane or vinyltriethoxysilane.

By coating the said powdered metal nitride with such keying agents the bond between the powder of the said metal nitride and the resin-forming material (or its cured resin) for medical or dental use is intensified, the property of the composite resin-forming material for medical or dental use is improved and the fluidity characteristic is improved when mixing the both and the filler content can be increased.

In the case of using the filler for medical or dental use belonging to the present invention by mixing to the resin-forming material (monomer) for medical or dental use into composite resin-forming material for medical or dental use, for proportions in which it is incorporated, the said filler should preferably be set at 50 - 95% by weight, and 70 - 90% by weight, in particular, and the resin-forming material for medical or dental use at 5 - 40% by weight, and 10 - 25% by weight, in particular. If the filler is used in the amount of less than 50% by weight, the composite resin obtained will be lowered in physical property values, such as compressive strength, abrasion strength and so on, whereas if it is in excess of 95% by weight, the composite resin paste in uncured condition will be higher in viscosity and inferior in operation.

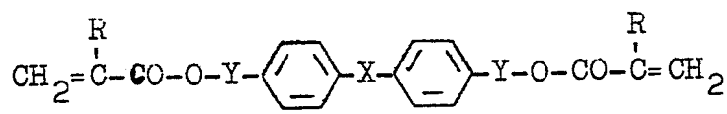
As the resin-forming material (monomer) for medical or dental use capable of using by mixing to

the metal nitride filler belonging to the present invention any conventionally known ones are available.

As such resin-forming material (monomer) for medical or dental use any ones are available which are conventionally known to be usable in this field. Their typical ones will be illustrated as follows.

(1) Polycarbinol polymethacrylates disclosed in the U.S. Patents 3,541,068 and 3,597,389, etc.:

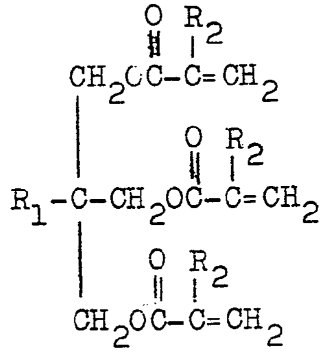
(2) 2,2-Bis-[p-(β-oxyethoxy)phenyl]-propane-dimethacrylate (hereinafter called the Bis-MEPP for short) type monomers represented by the following formula (4) as disclosed in the U.S. Patents 3,810,938; 3,923,740; 4,067,853, etc.:



... (4)

wherein
R stands for a hydrogen atom or a methyl group;
X stands for an alkylidene or a $-SO_2-$ group;
Y stands for an oxyalkylene group having between 2 and 5 carbon atoms or an alkylidene group containing between 1 to 5 carbon atoms.

(3) Trimethylolpropane trimethacrylate (TMPT) type monomers represented by the following formula (5) disclosed in British Patent 1,451,262:



..... (5)

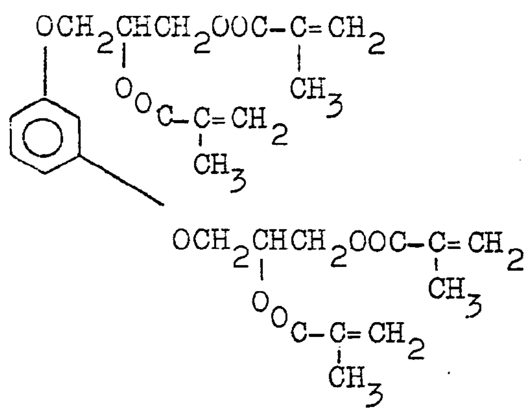
wherein R_1 is CH_3-, CH_3CH_2- or $CH_3CH_2CH_2-$, and R_2 is H or $-CH_3$.

(4) Urethane diacrylate type monomers represented by the following formula (6) as disclosed in the U.S. Patents, 3,825,518; 3,862,920, etc.:

$$CH_2=\overset{\overset{\Large R_1}{|}}{C}-COO-R_2-O\overset{\overset{\Large O}{\|}}{C}-NH-R_3-NH\overset{\overset{\Large O}{\|}}{C}O-R_2-OOC-\overset{\overset{\Large R_1}{|}}{C}=CH_2 \quad \ldots \ (6)$$

wherein R_1 is a hydrogen atom or a methyl group, R_2 is an alkylene group and R_3 is a divalent hydrocarbon radical.

(5) Monomers of the type represented by the following formula (7) as disclosed in the U.S. Patents 3,853,962, etc.:



..... (7)

(6) Neopentylglycol dimethacrylate (NPG) type monomers as disclosed in Japanese Laid-Open Patent Application (JAPAN KOKAI) No. 48-90332.

(7) Triethyleneglycol dimethacrylate (TEG) type monomers as disclosed in Japanese Laid-Open Patent Application (JAPAN KOKAI) No. 50-116581.

By formulating composite resin-forming material by combining together at least one member of compound (monomer) of the present invention represented by the said formulae (I), (II) and (III) and the said metal nitride (implant material) besides the said known resin-forming material (monomer) for medical or dental use it is possible to form composite resin compositions which are further improved in mechanical properties,

such as compressive strength, abrasion resistance and so on.

For a method of compounding of at least one member of compound (monomer) of the present invention represented by the formulae (I), (II) and (III) and the said metal nitride filler, preparation and curing of their paste, it is the same as described for the case of compounding the said compound (monomer) and conventional inorganic filler.

The composite resin-forming material using the filler-forming material for medical or dental use belonging to the present invention contains, in practical use, usually a catalyst for the polymerization of the resin-forming material and an activator for the formation of free radicals by the reaction of the catalyst besides the filler and the resin-forming material. Explanations were already given of these catalyst and activator.

For a method for use of such composite resin-forming material based on practical use, for instance, a paste-like substance (paste A) comprising the filler belonging to the present invention, preferably said powdery filler, resin-forming material (monomer) and an activator and a paste-like substance (paste B) comprising the filler belonging to the present invention, resin-forming material (monomer) and a catalyst could be better prepared in advance to mix together these two pastes when used by doctors or dentists. It can be used in good efficiency since the resin is cured with the polymerization initiated upon their mixing.

When using the said metal nitride of the present invention as filler, in some cases storage stability of the paste (paste B) may deteriorate according to the kind of the metal nitride if it is brought in contact with the catalyst for long.

In such cases, it is advantageous to use, as the filler for the paste A, metal nitride of the

present invention and as the filler for the paste B an inorganic filler capable of forming stable paste even if kept on in contact with conventionally known catalyst, such as powdered α-quartz, in such a manner that the metal nitride in the paste A should account for at least 50% by weight, preferably at least 70% by weight, and more preferably at least 80% by weight, based on the total amount of fillers including the inorganic filler in the paste B. By combining together the both pastes in such a manner a cured composite resin composition is formed therefrom which is stable to storage and extremely excellent in mechanical characteristics.

The composite resin composition which underwent curing treatment, using the filler for medical or dental use belonging to the present invention shows excellent mechanical strengths, such as extremely high compressive strength, abrasion resistance, impact resistance and so on, and is readily applicable according to usage to every fields of medical use, such as orthopedic surgery and restorative surgery field or operative dentistry and prosthetic dentistry field and so on.

The implant material of the present invention can be used alone and in addition, as a composite composition with any resin-forming material for medical or dental use. Not only that, but as mentioned earlier, even if used by mixing to self-curing compositions, such as silicate cement, zinc phosphate cement and so on, its physical property values, such as compressive strength, abrasion resistance and so on, can be improved.

The present invention will be specifically explained with the reference to working examples as follows. Unless otherwise specified, "part" and "%" in examples mean "part by weight" and "% by weight". Further, in examples the composition of the resin-forming material (monomer) and filler prior to curing

treatment is called the "composite resin" for short for convenience's sake.

In this connection, in examples the method for the preparation of composite resin and methods for the measurement of compressive strength, abrasion, water sorption, hardness, toothnrush abrasion, coloring, linear thermal expansion coefficient, and tensile strength follow the hereinafter-described procedures.

(1) A method for the preparation of composite resin:

(1)-1. Preparation of filler:

100 gr. of powdery filler classified to particle size of 50 microns or less was mixed to aqueous solution obtained by vigorously mixing 10 g of γ-methacryloxypropyltrimethoxysilane and 1 ml of acetic acid with agitation by addition of 200 ml of water and powdery filler was separated after agitation. Powdery filler so separated was dried in a hot air dryer held at 105°C for 24 hours whereby silane-treated filler was prepared.

In Examples filler was all treated with silane and used.

(1)-2. Preparation of monomer paste:

Monomer was divided into two equal parts, one monomer was incorporated with polymerization activator and filler prepared by following the procedure of (1)-1 above (hereinafter called Paste A for short) and the other monomer was incorporated with catalyst and filler prepared by following the procedure of (1)-1 (hereinafter called Paste B for short).

In Examples, N,N-bis-(2-hydroxyethyl)-4-methylaniline was used as activator and benzoyl peroxide as catalyst.

For the amount in which the activator was mixed to Paste A and the amount in which the catalyst was mixed to Paste B they were formulated in such a manner that curing should occur about 3 minutes after mixing Paste A and Paste B.

(1)-3. Preparation of composite resin:

Paste A and Paste B were taken each in equal amounts, mixed and kneaded together on kneading paper at room temperature for 30 seconds whereby composite resin was prepared.

(2) Measurement of compressive strength:

Based on American Dental Association (ADA) Specification No. 9 for Dental Silicate Cement compressive strength was measured by the following procedures.

Composite resin was loaded in a mould, sealed with sheeted glass, then placed in a pressure vessel and left to stand under an atmosphere of 37°C and relative humidity of 100% for 15 minutes. The cured composite resin was taken out from the mould and immersed in water held at 37°C for 24 hours whereby specimens were prepared. By using Instron tester specimens were pressed at conditions of press rate of 0.2 mm/min. to determine their compressive strength.

(3) Measurement of abrasion loss:

Cured composite resin loaded in and taken out from the mould by following the procedures set forth in section of "(2) Measurement of compressive strength" was used as specimens for measurement of abrasion loss. The specimens were dried in a hot air dryer held at 100°C for 24 hours and then cooled in a desiccator for one hour and weighed. The specimens were placed in a cylindrical metal ball mill with an inner capacity of 500 ml and inner diameter of 10 cm and simultaneously, 20 stainless steel balls 1 mm across and 200 ml of polishing paste prepared by adding 900 parts by weight of distilled water to 200 parts by weight of powdered Si_3N_4 passing through a 325 mesh sieve as polishing material were loaded, sealed and then rotated at a rate of 100 r.p.m. for 78 hours. After it was finished, the specimens were washed with water, dried in the hot air dryer held at 100°C for 24 hours and cooled in the desiccator for another one hour and weighed. Abrasion loss was calculated according to the following equation:

$$\text{Abrasion loss } (cm^3) = [(\text{weight of unpolished specimens}) - (\text{weight of polished specimens})] / (\text{density of specimens})$$

(4) Measurement of amount of water sorption:

Based on American Dental Association (ADA) Specification No. 27 for Direct Filling Resins the amount of water absorbed was measured by the following procedure.

Composite resin was cured to prepare a disk

specimen 20 mm across and 1 mm thick. The specimen was left to stand in a constant temperature dryer held at 37°C, then placed in the desiccator, cooled for one hour and weighed. Value when a constant quantity was reached with repetition of this operation was set as dry weight. Then, the specimen was immersed in water held at 37°C for 7 days, then taken out, water on the surface was wiped off with soft gauze and the specimen was weighed to determine the weight of water absorbed. The amount of water absorbed was calculated by the following equation:

$$\underset{(\mathrm{mg/cm^2})}{\text{Amount of water sorption}} = \big((\text{weight after immersion}) - (\text{conditioned weight})\big) / \text{surface area of specimen}$$

(5) Measurement of hardness:

Measurement was made of Knoop hardness by means of microhardness tester of Shimazu make. Composite resin was cured to prepare a columnar specimen 10 mm across and 5 mm high and a load of 900 g was carried on the flat surface of the specimen for 15 minutes. The length of dent formed on the surface of the specimen was measured to determine Knoop hardness.

(6) Toothbrush abrasion test:

Composite resin was cured to prepare and fix a columnar specimen 13 mm across and 4 mm high. A commercially available toothbrush with a load of 200 g was applied to the flat portion of the specimen and this toothbrush was reciprocated at a stroke of 2 reciprocations/second to polish the specimen surface. In the meantime, solution prepared by diluting 150 g of commercially available toothpaste to 1/2 with water was continuously added dropwise. After 8 hours the specimen was washed with water, dried and weighed. Rate of toothbrush abrasion loss was calculated by the following equation.

$$\text{Rate of toothbrush abrasion loss (\%)} = \frac{(\text{weight of specimen before abrasion}) - (\text{weight of specimen after abrasion})}{(\text{weight of specimen before abrasion})} \times 100$$

(7) Coloring test:

Disked test pieces 13 mm across and 4 mm high were surface-polished with No. 800 emery paper and then immersed in commercially available aqueous coffee solution (solution obtained by dissolving 2.5 g of powdered coffee in 100 ml of water) at 37°C for 4 days. The specimens were washed with water, dried and then their color was measured by means of colorimeter, a product of Nippon Denshoku Kogyo company, to read values L, a and b. Likewise, values L_0, a_0 and b_0, measured color values of the specimen surfaces prior to immersing into the coffee solution were read, the degree of discoloration ΔE was calculated by the following equation and ΔE was set as a basis for coloring. The greater the ΔE, the greater is the degree of discoloration. This test was also effected on the surface of the unpolished specimen.

$$\Delta E = \sqrt{(L-L_0)^2+(a-a_0)^2+(b-b_0)^2}$$

(8) Measurement of linear thermal expansion coefficient:

Composite resin was enclosed in a glass tube 5 mm in diameter and 20 mm in length, the opening of the tube was sealed with cover glass for microscope, left to stand at room temperature for 15 minutes and then cured composite resin was taken out from the glass tube whereby specimens for measurement were prepared.

Measurement was made of the linear thermal expansion coefficient of the specimens so prepared by means of linear thermal expansion measuring instrument, a product of Rigsku Denki company. In making measurement heating and temperature rasing rate was set at 5°C/min.

(9) Measurement of tensile strength:

Based on pressure tear test according to ADA Specification No. 27 for the diametrial method tensile strength was measured by the following procedure.

Composite resin was loaded in a stainless steel mould 6 mm in inner diameter and 3 mm in height and the opening of the mould was sealed with cover glass for

microscope. The mould was left to stand under an atmosphere of 37°C and relative humidity of 95% for 15 minutes. After that, the cured composite resin was taken out from the mould. This cured composite resin was polished by use of powdered SiC and then immersed in the water held at 37°C for 24 hours whereby specimens for measurement were prepared.

Tensile strength of the specimens so prepared was measured by means of Instron tension tester. In making measurement head press rate was set at 1 cm/min.

Example 1:

Silane-treated α-SiO_2 was prepared following the procedure for the preparation of filler in section (1)-1. Then, using mixed monomer, as the monomer, prepared by mixing tetramethylolmethane triacrylate (TMM-3A) and tetramethylolmethane tetracrylate (TMM-4A) in proportions of 55:45 (by weight ratio), silane-treated α-SiO_2, catalyst and activator, the mixed monomer was divided into two equal parts for the preparation of Paste A1-1 and Paste B1-1 of following compositions according to the procedure for the preparation of monomer paste in section (1)-2.

Paste A1-1 and Paste B1-1 so prepared were taken each in equal amounts, mixed and kneaded together on kneading paper at room temperature for 30 seconds whereby composite resin was prepared.

This composite resin was loaded in a stainless steel pipe with inner diameter of 10 mm and height of 5 mm at one end and excess part was removed off with sheeted glass. An injection needle was stuck into the surface of the composite resin at intervals of 10 seconds at room temperature to measure the curing time. It was about 3 minutes long.

Paste A1-1	Part by weight
Tetramethylolmethane triacrylate (TMM-3A)	55
Tetramethylolmethane tetracrylate (TMM-4A)	45
Silane treated α-SiO_2	300
N,N-bis-(2-hydroxyethyl)-4-methylaniline	0.8

Paste B1-1	Part by weight
Tetramethylolmethane triacrylate (TMM-3A)	55
Tetramethylolmethane tetracrylate (TMM-4A)	45
Silane treated α-SiO_2	300
Benzoyl peroxide	0.8

Compressive strength, abrasion loss and bonding strength were measured of the composite resin and results were shown in Table 1.

Paste A's and Paste B's of following compositions were formulated using various monomers conventionally known as resin-forming material for medical or dental use instead of the mixed monomer of TMM-3A and TMM-4A.

Paste A1-2	Part by weight
Bisphenol A diglycidyl methacrylate (Bis-GMA)	80
Triethyleneglycol dimethacrylate (TEGDMA)	20
Silane treated α-SiO_2	300
N,N-bis(2-hydroxyethyl)-4-methylaniline	0.8

Paste B1-2	Part by weight
Bisphenol A diglycidyl methacrylate (Bis-GMA)	80
Triethyleneglycol dimethacrylate (TEGDMA)	20
Silane treated α-SiO_2	300
Benzoyl peroxide	0.8

Paste A1-3	Part by weight
Bismethacryloxyethoxydiphenylpropane (Bis-MEPP)	100
Silane treated α-SiO_2	300
N,N-bis(2-hydroxyethyl)-4-methylaniline	1.0

Paste B1-3	Part by weight
Bismethacryloxyethoxydiphenylpropane (Bis-MEPP)	100
Silane treated α-SiO_2	300
Benzoyl peroxide	1.0

Paste A1-4	Part by weight
Neopentylglycol dimethacrylate (NPGDMA)	100
Silane treated α-SiO_2	300
N,N-bis(2-hydroxyethyl)-4-methylaniline	2.0

Paste B1-4	Part by weight
Neopentylglycol dimethacrylate (NPG-DMA)	100
Silane treated α-SiO_2	300
Benzoyl peroxide	2.0

Paste A1-5	Part by weight
Trimethylolpropane triacrylate (TMPT)	100
Silane treated α-SiO_2	300
N,N-bis(2-hydroxyethyl)-4-methylaniline	1.5

Paste B1-5	Part by weight
Trimethylolpropane triacrylate (TMPT)	100
Silane treated α-SiO_2	300
Benzoyl peroxide	1.5

These Paste A's and Paste B's corresponding to sub-numbers were taken each in equal amounts and various composite resins were prepared following the same procedures as the above. Compressive strengths, abrasion loss and bonding strengths were measured of these cured composite resins. Results were shown in Table 1:

Table 1

	Monomer composition tested *1	Amount of filler used *2 (α-SiO_2)	Compressive strength (kg/cm^2)	Abrasion loss (cm^3)	Bonding strength (kg/cm^2)	
					Bovine enamel	Bovine dentin
1	TMM-3A(55)/TMM-4A(45)	75 wt.%	2,570	0.49	60-70	15-20
2*	Bis-GMA(80)/TEG(20)	"	2,100	0.62	30-40	0-5
3*	Bis-MEPP	"	2,290	0.59	-	-
4*	MPGDMA	"	2,180	0.57	-	-
5*	TMPT	"	2,440	0.62	5-10	0

NOTE) *1 In the case of mixed monomer, parentheses ( ) following upon a short form for each monomer indicates a weight ratio of the monomer. (The same will apply to the respective tables in the hereinafter-described Examples.)

*2 The amount of filler used indicates a percentage by weight of the filler based on the total amount of the monomer and the filler. (The same will apply to the respective tables in the hereinafter-described Examples.)

* Indicates Control and the same will apply to the respective tables in the hereinafter-described Examples.

It follows from the above table that the composite resin (Run No. 1) comprising the monomer composition of TMM-3A(55)/TMM-4A(45) belonging to the present invention should be excellent in either of compressive strength, abrasion loss and bonding strength as compared to the composite resins of Run Nos. 2 - 5 comprising the monomer compositions of Bis-GMA/TEG, Bis-MEPP, MPGDMA or TMPT conventionally known as the resin-forming monomer for medical or dental use.

Bonding strength was measured by the following procedure.

(1) Bonding strength to bovine dentin:

A fresh anterior bovine tooth implanted into a square rod made of acryl resin was polished with emery paper until the dentin exposed itself, and further polished and finished with No. 800 emery paper for the formation of a contact surface whereby there was prepared a testpiece of material for the bonding test with the bovine dentin. This bonding testpiece was stored in water. It was taken out from the water immediately before the measurement was made. The surface of the testpiece was well wiped off and further dried in a weak air stream. Then, the bonding surface of the bovine dentin was coated with composite resin and the square rod made of acryl resin was stuck and pressed against the coated surface. It was left to stand at room temperature for 15 minutes and then immersed in the water held at 37°C. for 24 hours. Both ends of the acryl resin square rods of the specimen were pulled apart at a rate of 1 mm/min. to determine the bonding strength. The bonding strength was indicated by the maximum value and the minimum value of measured numericals when measuring the respective specimens for every 20 testpieces.

(2) Bonding strength to bovine enamel:

A fresh anterior bovine tooth implanted in a square rod made of acryl resin was polished and leveled with emery paper, and further polished and finished with

No. 800 emery paper for the formation of a bonding surface whereby there was prepared a testpiece of material for the bonding test with the bovine enamel. This bonding testpiece was stored in water. It was taken out from the water immediately before the measurement was made. The surface of the testpiece was well wiped off and etched with 50% aqueous phosphate solution for one minute. It was successively washed with water and air dried using a weak air stream. Using the testpiece of material for the bonding test with the bovine enamel so prepared its bonding strength was measured following the same procedure as in the case of the measurement of the bonding strength with the bovine dentin and the measured values were indicated in the same manner.

Example 2:

Using, as the monomer, mixed monomers prepared by mixing TMM-3A and TMM-4A in various such proportions as indicated in Table 2, Paste A 2 and Paste B 2 of following compositions were prepared. Paste A 2 and Paste B 2 were mixed and kneaded together following the same procedure as set forth in Example 1 whereby composite resins were prepared.

Paste A 2	Part by weight
TMM-3A } TMM-4A }	100 in total
Silane treated α-SiO_2	300
N,N-bis(2-hydroxyethyl)-4-methylaniline	0.1

Paste B 2	Part by weight
TMM-3A } TMM-4A }	100 in total
Silane treated α-SiO_2	300
Benzoyl peroxide	1.0

Compressive strength, abrasion loss, amount of water sorption and bonding to bovine tooth were measured of these cured composite resins. Results were shown in Table 2.

Table 2

	Monomer composition		Amount of filler used (α-SiO_2)	Compressive strength (kg/cm^2)	Abrasion loss (cm^3)	Amount of water sorption (mg/cm^2)	Bonding strength (kg/cm^2) (to bovine dentin)
	TMM-3A	TMM-4A					
1	100	0	75 wt.%	2,410	0.55	0.38	15-20
2	90	10	"	2,480	0.54	0.36	15-20
3	70	30	"	2,490	0.50	0.30	10-15
4	50	50	"	2,520	0.48	0.30	10-15
5	30	70	"	2,550	0.48	0.33	5-10
6	10	90	"	2,500	0:52	0.33	5-10
7	0	100	"	2,450	0.53	0.37	0-5

It is noted from the above table that either triacrylate (TMM-3A) or tetracrylate (TMM-4A) will suffice for the monomer constituting the composite resin of the present invention. The bonding strength value increases in proportion to increased amount of TMM-3A mixed. For this reason it is conceived that TMM-3A possesses another methylol group ($-CH_2OH$) besides the triacrylate ester and this methylol group contributes to the bonding with the hard tissue of the human body.

In the case of the mixed monomer using a combination of TMM-3A and TMM-4A and the mixed monomer prepared by mixing them together in proportions of 30-70 parts by weight of TMM-3A and 70-30 parts by weight of TMM-4A, in particular dental composite resin could be advantageously formed which is excellent in the bonding with the hard tissue of the human body with excellent compressive strength.

In the case, further, of using TMM-3A and TMM-4A in combination, composite resin formed therefrom is found to show very excellent water resistance besides the said characteristics.

Example 3:

Composite resins were prepared following the same procedures of Example 1 except that there were used the mixed monomer of TMM-3A(55)/TMM-4A(45) belonging to the present invention or conventionally known mixed monomer of Bis-GMA(80)/TEG(20) as the resin-forming monomer, given amounts of various inorganic metal oxides conventionally known as the dental inorganic filler listed in Table 3 below as the filler, catalyst and activator in such amounts as set forth in the Table 3. Comparative strength and abrasion loss were measured of these cured composite resins. Results were tabulated in Table 3.

Table 3

	Monomer composition	Filler		Amount of activator (part/100 parts of monomer)	Amount of catalyst (part/100 parts of monomer)	Compressive strength (kg/cm^2)	Abrasion loss (cm^3)
		Kind	Amount (wt %)				
1	TMM-3A(55)/TMM-4A(45)	Al_2O_3	75	0.8	1.0	2,570	0.47
2	"	ZrO_2	70	1.0	1.5	2,500	0.47
3	"	$ZrSiO_4$	75			2,700	0.43
4*	Bis-GMA(30)/TEG(20)	Al_2O_3	75	0.8	1.0	2,100	0.60
5*	"	ZrO_2	70			2,040	0.58
6*	"	$ZrSiO_4$	75			2,200	0.55

* indicates Control.

It is noted from the above table that if various metal oxides conventionally known as dental inorganic filler are to be used in combination with conventionally known Bis-GMA type monomers, they will not be fully satisfactory in the point of compressive strength and abrasion resistance, whereas the monomer belonging to the present invention, even if used in combination with these metal oxides, will show fully satisfactory compressive strength and abrasion resistance.

Example 4:

Using, as the composite resin-forming monomer, TMM-3A(55)/TMM-4A(45) or tetramethylolmethane trimethacrylate (TMM-3M)(55)/tetramethylolmethane tetramethacrylate (45) Paste A 4-1, B 4-1 and Paste A 4-2 and B 4-2 of following compositions were prepared. Following the same procedure as that of Example 1 these pastes were mixed for the preparation of composite resins.

Paste A 4-1	Part by weight
TMM-3A	55
TMM-4A	45
Silane treated α-SiO_2	456
N,N-bis(2-hydroxyethyl)-4-methylaniline	0.8

Paste B4-1	Part by weight
TMM-3A	55
TMM-4A	45
Silane treated α-SiO_2	456
Benzoyl peroxide	1.0

Paste A 4-2	Part by weight
Tetramethylolmethane trimethacrylate (TMM-3M)	55
Tetramethylolmethane tetramethacrylate (TMM-4M)	45
Silane treated α-SiO_2	456
N,N-bis(2-hydroxyethyl)-4-methylaniline	0.8

Paste B 4-2	Part by weight
Tetramethylolmethane trimethacrylate (TMM-3M)	55
Tetramethylolmethane tetramethacrylate (TMM-4M)	45
Silane treated α-SiO_2	456
Benzoyl peroxide	1.0

Compressive strength, abrasion loss and amount of water sorption were measured of these cured composite resins results were tabulated in Table 4.

Table 4

	Monomer composition	Amount of filler used (α-SiO_2)	Compressive strength (kg/cm^2)	Abrasion loss (cm^3)	Amount of water sorption (mg/cm^2)
1	TMM-3A(55)/TMM-4A(45)	82 wt%	2,850	0.43	0.28
2	TMM-3M(55)/TMM-4M(45)	"	2,870	0.40	0.29

It follows from the above table that if TMM-3M (55)/TMM-4M(45) is to be substituted for TMM-3A(55)/ TMM-4A(45) as the composite resin-forming monomer, dental material obtained will have equally excellent physical properties in the compressive strength, abrasion loss and amount of water sorption. That is, it is noted there that not only tetramethylolmethane tri- or tetra-acrylate but tetramethylolmethane tri- or tetra-methacrylate should also be preferred as the composite resin-forming monomer of the present invention.

Example 5:

Using, as the composite resin-forming monomer, mixed monomers comprising a combination of TMM-3A and TMM-4A belonging to the present invention and conventionally known dental resin-forming monomers Paste A 5-1, B 5-1 and Paste A 5-2 and B 5-2 were prepared. Following the same procedure as that of Example 1 these pastes were mixed for the preparation of composite resins.

Paste A 5-1	Part by weight
TMM-3A	50
TMM-4A	30
Bis-MEPP	13
NPGDMA	7
N,N'-bis(2-hydroxyethyl)-4-dimethylaniline	1.0
Silane treated α-SiO_2	456

Paste B 5-1	Part by weight
TMM-3A	50
TMM-4A	30
Bis-MEPP	13
NPGDMA	7
Silane treated α-SiO_2	456
Benzoyl peroxide	1.2

Paste A 5-2	Part by weight
TMM-4A	80
Bis-GMA	10
NPGDMA	10
N,N-bis(2-hydroxyethyl)-4-methylaniline	0.8
Silane treated α-SiO_2	456

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Paste B 5-2	Part by weight
TMM-4A	80
Bis-GMA	10
NPGDMA	10
Benzoyl peroxide	1.0
Silane treated Si_3N_4	456

Compressive strength and abrasion loss were measured of these cured composite resins and results were tabulated in Table 5.

Table 5

	Monomer composition	Amount of filler used (α-SiO_2)	Compressive strength (kg/cm^2)	Abrasion loss (cm^3)
1	TMM-3A(50)/TMM-4A(30)/Bis-MEPP(13)/NPG(7)	82 wt%	2,860	0.43
2	TMM-4A(80)/Bis-GMA(10)/NPG(10)	"	2,840	0.41

It is noticed from the above table that the cured composite resins using mixed monomers prepared by mixing about 20% by weight of conventionally known dental resin-forming monomers, such as Bis-MEPP, NPG, Bis-GMA and so on, to the composite resin-forming monomer belonging to the present invention should also be valuable as dental material in terms of their physical property values. They did not give rise to any compatibility problem.

Example 6:

Following the procedure for the preparation of filler in section (1)-1 there were prepared various silane-treated inorganic fillers as mentioned in the following Table 6. Then, using, as the composite resin-forming monomer, mixed monomers prepared by mixing conventionally known bisphenol A diglycidyl methacrylate (bis-GMA) and triethyleneglycol dimethacrylate (TEG) in proportions of 80:20 (by weight ratio), silane-treated inorganic filler, catalyst and activator, Paste A-6 and Paste B-6 of following compositions were prepared

following the procedure for the preparation of monomer paste in section (1)-2.

Paste A-6 and Paste B-6 were taken each in equal amounts, mixed and kneaded together on kneading paper at room temperature for 30 seconds for the preparation of composite resins.

This composite resin was loaded in a stainless steel pipe with inner diameter of 10 mm and height of 5 mm at one end and excess part was removed off with sheeted glass. Then, an injection needle was stuck into the surface of the composite resin at intervals of 10 seconds at room temperature to determine the curing time. It was about 3 minutes long.

The filler used was of powder form with particle size of 50 microns or less. Paste A was incorporated with N,N-bis-(2-hydroxyethyl)-4-methylaniline as the polymerization activator and Paste B was incorporated with benzoyl peroxide as the catalyst and 2,5-di-tért, butyl-4-methylphenyl (BHT) as the polymerization inhibitor.

Paste A	Part by weight
Bis-GMA(80)/TEGDMA(20)	100
N,N-bis-(2-hydroxyethyl)-4-methylaniline	2
Silane treated inorganic filler	400

Paste B	Part by weight
Bis-GMA(80)/TEGDMA(20)	100
Benzoyl peroxide	2.5
BHT	0.25
Silane treated inorganic filler	400

Compressive strength and abrasion loss were measured of this cured composite resin. Results were tabulated in Table 6.

Table 6

	Monomer composition *1	Filler			Compressive strength (kg/cm^2)	Abrasion loss (cm^3)
		Kind	Mohs' hardness	Amount *2 (wt%)		
1	Bis-GMA(80)/TEG(20)	Si_3N_4	9<	80	2,750	0.27
2	"	AlN	7 - 8	"	2,570	0.33
3	"	BN	9<	"	2,800	0.26
4	"	VN	9	"	2,660	0.28
5*	"	α-SiO_2	7	"	2,260	0.60
6*	"	Al_2O_3	9	"	2,260	0.56

* indicates Control.

NOTE) *1 In the case of mixed monomer parentheses ( ) following upon a short form for each monomer indicates a weight ratio of the monomer.

*2 The amount of filler used indicates a weight percentage of filler based on the total amount of the monomer and the filler.

It follows from the above table that the composite resins (Run Nos. 5 and 6) comprising a combination of Bis-GMA/TEG conventionally known as the composite resin-forming monomer for medical or dental use and powdered alumina filler having exceptionally high hardness and abrasion resistance among conventionally known fillers (with a Mohs' scale of hardness of 9) or most widely used α-SiO_2 are still far from satisfactory in the compressive strength and abrasion resistance, but the composite resins (Run Nos. 1 - 4) in combination with the filler which is comprised of metal nitride belonging to the present invention and which is 7 or more in the Mohs' scale of hardness have markedly high compressive strength and abrasion resistance.

Example 7:

Pastes of following compositions were prepared using, as the composite resin-forming monomer, conventionally known bismethacryloxyethoxyphenylpropane (Bis-MEPP), neopentylglycol dimethacrylate (NPG) and trimethylolpropane triacrylate (TMPT) and as the filler, conventionally most widely used α-SiO_2 or Si_3N_4 belonging to the present invention. Following the same procedure as that of Example 6 these pastes were mixed and kneaded together for the preparation of composite resins.

Paste A 7-1	Part by weight
Silane treated filler	400
Bis-MEPP	100
N,N-bis-(2-hydroxyethyl)-4-methylaniline	1.0

Paste B 7-1	Part by weight
Silane treated filler	400
Bis-MEPP	100
Benzoyl peroxide	2.0
BHT	0.15

Paste A 7-2	Part by weight
Silane treated filler	400
NPGDMA	100
N,N-bis-(2-hydroxyethyl)-4-methylaniline	2.0

Paste B 7-2	Part by weight
Silane treated filler	400
NPGDMA	100
Benzoyl peroxide	2.5
BHT	0.10

Paste A 7-3	Part by weight
Silane treated inorganic filler	400
TMPT	100
N,N-bis-(2-hydroxylethyl)-4-methylaniline	1.5

Paste B 7-3	Part by weight
Silane treated inorganic filler	400
TMPT	100
Benzoyl peroxide	2.5
BHT	0.15

Compressive strength and abrasion loss were measured of these cured composite resins. Results were tabulated in Table 7.

Table 7

	Monomer	Filler		Compressive strength (kg/cm^2)	Abrasion loss (cm^3)
		Kind	Amount (wt %)		
1	Bis-MEPP	Si_3N_4	80	2,890	0.24
2	NPGDMA	"	"	2,930	0.25
3	TEPT	"	"	3,000	0.23
4*	Bis-MEPP	α-SiO_2	"	2,410	0.58
5*	NPGDMA	"	"	2,450	0.57
6*	TMPT	"	"	2,470	0.57

The above table shows that in comparison with composite resins (Run Nos. 4 - 6) comprising a combination of Bis-MEPP, NPGDMA or TEPT conventionally known as the composite resin-forming monomer for medical or dental use and conventionally known filler α-SiO_2, the composite resins (Run Nos. 1 - 3) comprising a combination of these conventionally known monomers and Si_3N_4, the filler

belonging to the present invention, should have much higher compressive strength and abrasion resistance.

Example 8:

Using, as the composite resin-forming monomer, mixed monomer prepared by mixing TMM-3A and TMM-4A belonging to the present invention in proportions of 55:45 (by weight ratio) and as the powdery filler, conventionally known metal oxide or metal nitride belonging to the present invention in such given amounts as indicated in the following Table 8 Paste A 8 and Paste B 8 of following compositions were prepared.

Paste A 8	Part by weight
Various powdery fillers	in given amounts as indicated in Table 8
TMM-3A(55)/TMM-4A(45)	100
N,N-bis-(2-hydroxyethyl)-4-methylaniline	2

Paste B 8	Part by weight
Various powdery fillers	in given amounts as indicated in in Table 8
TMM-3A(55)/TMM-4A(45)	100
Benzoyl peroxide	2.5
BHT	0.15

Compressive strength and abrasion loss were measured of these cured composite resins. Results were tabulated in Table 8.

Table 8

	Monomer composition	Filler			Compressive strength (kg/cm2)	Abrasion loss (cm3)
		Kind	Mohs' hardness	Amount (wt%)		
1	TMM-3A(55)/TMM-4A(45)	Si_3N_4	9<	75	3,080	0.22
2	"	α-SiO_2	7	"	2,570	0.49
3	"	Al_2O_3	9	"	2,570	0.47
4	"	Si_3N_4	9<	80	3,200	0.19
5	"	AlN	7 - 8	"	2,980	0.25
6	"	ZrN	8 - 9	"	3,010	0.23
7	"	NbN	8	"	2,860	0.25
8	"	TiN	8 - 9	"	3,020	0.24
9	"	BN	9<	"	3,280	0.16
10	"	VN	9	"	3,140	0.20
11	"	α-SiO_2	7	"	2,720	0.46
12	"	Al_2O_3	9	"	2,720	0.45

It follows from the above table that when making comparisons of compressive strength and abrasion loss between the cured composite resins (Run Nos. 2, 3, 11 and 12) prepared by combining α-SiO_2 or Al_2O_3 being conventionally known filler with TMM-3A(55)/TMM-4A(45) being the monomer of the present invention and the cured composite resins (Run Nos. 1, 4 - 10) in combination with the metal nitride with a Mohs' scale of hardness of 7 or more, the filler of the present invention, the latter ones should be more better in any of the compressive strength and abrasion loss.

It is also noted there that with the cured composite resins using, as the filler, the metal nitride belonging to the present invention BN, VN and Si_3N_4 with a Mohs' scale of hardness of 9 or more show exceptionally high compressive strength and abrasion resistance and that they should be suited to use as crown bridge restoratives or filling materials in molars.

It also follows from comparisons between Run Nos. 1 and 4, between Run Nos. 2 and 11 and between Run Nos. 3 and 12 that the compressive strength and abrasion resistance both are enhanced in proportions to the amount of filler used.u

Example 9:

Composite resins were prepared following the same procedure as that of Example 6 except that there were used, as the composite resin-forming monomer, TMM-3A (55)/TMM-4A(45) belonging to the present invention, conventionally known Bis-GMA(80)/TEGDMA(20) and TMM-3A(44)/ TMM-4A(36)/Bis-MEPP(20), as the powdery filler, those fillers mentioned in the following Table 9 in given amounts and further, the activator and the catalyst each in given amounts mentioned in the Table 9. Compressive strength and abrasion loss were measured of these cured composite resins. Results were tabulated in Table 9.

Table 9

	Monomer composition	Filler		Amount of activator (part/200 parts of monomer)	Amount of catalyst (part/200 parts of monomer)	Compressive strength (kg/cm^2)	Abrasion loss (cm^3)
		Kind	Amount (wt %)				
1	TMM-3A(55)/TMM-4A(45)	SiN_4	85	2.0	2.5	3,350	0.16
2	"	"	90	"	"	3,520	0.14
3	"	ZrN	80	"	"	3,010	0.23
4	"	TiN	"	"	"	3,020	0.24
5	TMM-3A(44)/TMM-4A(36)/Bis-MEPP(20)	SiN_4	"	1.0	2.0	3,220	0.17
6*	Bis-GMA(80)/TEG(20)	α-SiO_2	"	2.0	2.5	2,260	0.60

* BHT was used in the amount of 0.15 (part/200 parts of monomer) in Run Nos. 1 - 5 and in the amount of 0.25 (part/200 parts of monomer) in Run No. 6.

In comparison in compressive strength as well as in abrasion loss with the cured composite resin (Run No. 6) with a combination of conventionally known monomer Bis-GMA(80)/TEG(20) and known filler α-SiO_2 a first glance at the above table shows that by making composite resin-forming material by combining the monomer containing 80% or more of TMM-3A(55)/TMM-4A(45), the monomer of the present invention, with SiN_4, ZrN or TiN, the metal nitride, the composite resin formed should have specifically excellent compressive strength and abrasion resistance.

When comparing amounts in which the filler can be combined with the composite resin-forming monomer in such a range as not to give rise to the operation problem of the composite resin paste, the monomer containing 80% or more of TMM-3A(55)/TMM-4A(45), the monomer of the present invention, could be incorporated with the filler in greater amounts than the Bis-GMA(80)/TEG(20). This is conceived to be attributed to the difference in the fluid characteristics of the monomer. As clear from a comparison between Run No. 1 and Run No.2, because of compressive strength and abrasion resistance increasing in proportion to the amount of filler used, obviously the composite resin having more high compressive strength and abrasion resistance could be obtained when using, as the composite resin-forming material, the monomer of the present invention capable of incorporating with a great deal of filler without causing trouble in the operation.

Example 10:

Composite resins were prepared following the same procedure as that of Example 6, using, as the composite resin-forming monomer, TMM-3A(55)/TMM-4A(45) or Bis-GMA(80)/TEGDMA(20) and as the powdery filler, single compounds or mixtures of various fillers mentioned below.

The following are compositions of the respective pastes used in the preparation of composite resins.

Paste A 10-1	Part by weight	Paste B 10-1	Part by weight
TMM-3A(55)/TMM-4A(45)	100	TMM-3A(55)/TMM-4A(45)	100
Si_3N_4	400	α-SiO_2	400
N,N-bis-(2-hydroxyethyl)-4-methylaniline	2	Benzoyl peroxide	2.5
		BHT	0.15

Paste A 10-2	Part by weight	Paste B 10-2	Part by weight
TMM-3A(55)/TMM-4A(45)	100	TMM-3A(55)/TMM-4A(45)	100
Si_3N_4	400	Al_2O_3	400
N,N-bis-(2-hydroxyethyl)-4-methylaniline	2	Benzoyl peroxide	2.5
		BHT	0.15

Paste A 10-3	Part by weight	Paste B 10-3	Part by weight
TMM-3A(55)/TMM-4A(45)	100	TMM-3A(55)/TMM-4A(45)	100
Si_3N_4	400	Si_3N_4	400
N,N-bis-(2-hydroxyethyl)-4-methylaniline	2	Benzoyl peroxide	2.5
		BHT	0.15

Paste A 10-4	Part by weight	Paste B 10-4	Part by weight
Bis-GMA(80)/TEGDMA(20)	100	Bis-GMA(80)/TEGDMA(20)	100
Si_3N_4	400	α-SiO_2	400
N,N-bis-(2-hydroxyethyl)-4-methylaniline	2	Benzoyl peroxide	2.5
		BHT	0.25

Paste A 10-5	Part by weight	Paste B 10-5	Part by weight
Bis-GMA(80)/TEGDMA(20)	100	Bis-GMA(80)/TEGDMA(20)	100
α-SiO_2	400	α-SiO_2	400
N,N-bis-(2-hydroxyethyl)-4-methylaniline	2	Benzoyl peroxide	2.5
		BHT	0.25

Table 10

	Monomer composition	Filler		Compressive strength (kg/cm^2)	Abrasion loss (cm^3)
		Kind	Amount (wt %)		
1	TMM-3A(55)/TMM-4A(45)	Si_3N_4 α-SiO_2	40 40	2,960	0.33
2	"	Si_3N_4 Al_2O_3	40 40	2,975	0.32
3	"	Si_3N_4	80	3,200	0.19
4	Bis-GMA(80)/TEGDMA(20)	Si_3N_4 α-SiO_2	40 40	2,505	0.44
5*	"	α-SiO_2	80	2,260	0.60

It is noted from the above table that in comparison of the composite resin (Run No. 5) with a combination of Bis-GMA(80)/TEGDMA(20), the conventionally known composite resin (Run No. 4) comprising the said monomer and the known filler α-SiO_2 of which the half the amount was replaced by Si_3N_4, the filler of the present invention, with the cured composite resin formed by use of only a small amount of the filler of the present invention the filler is very great in the extent in which it contributes to the improvements of the compressive strength and abrasion resistance.

It is also noted from a comparison between Run No. 4 and Run No. 1 that the monomer of the present invention should bring about greater effect on the improvement of the compressive strength and abrasion resistance.

It follows from a comparison between Run No. 5 and Run No. 3 that if the monomer of the present invention and the filler of the present invention are to be substituted for the known monomer and the known filler, the

compressive strength and abrasion resistance will be much more improved.

Furthermore, as the result of testing the stability of these pastes for the preparation of composite resins, those prepared by incorporating the metal nitride of the present invention into Paste B went more or less bad in the storage stability as compared to those in which conventionally known α-SiO_2 or Al_2O_3 was incorporated. Even in such cases, it is noted that by using the metal nitride of the present invention as the filler for Paste A and conventionally known filler, such as α-SiO_2 and so on, as the filler for Paste B and combining together these both pastes the cured composite resin obtained will be stabilized in storage and markedly excellent in mechanical characteristics.

Example 11:

TMM-3A/TMM-4A, the typical example of the present invention, and conventionally known Bis-GMA/TEG, as the composite resin-forming monomer and Si_3N_4 of the present invention, and conventionally known α-SiO_2, as the filler were chosen and these monomers and fillers were combined together for the preparation of 4 types each of pastes —— Paste A 11-1 to A 11-4 and Paste B 11-1 to B 11-4 —— were prepared.

Paste A 11-1	Part by weight
TMM-3A	55
TMM-4A	45
N,N-bis-(2-hydroxyethyl)-4-methylaniline	0.6
Silane treated Si_3N_4	400

Paste B 11-1	Part by weight
TMM-3A	55
TMM-4A	45
Benzoyl peroxide	0.8
Silane treated Si_3N_4	400

Paste A 11-2	Part by weight
TMM-3A	55
TMM-4A	45
N,N-bis-(2-hydroxyethyl)-4-methylaniline	0.6
Silane treated α-SiO_2	400

Paste B 11-2	Part by weight
TMM-3A	55
TMM-4A	45
Benzoyl peroxide	0.8
Silane treated α-SiO_2	400

Paste A 11-3	Part by weight
Bis-GMA	80
TEGDMA	20
N,N-bis(2-hydroxyethyl)-4-methylaniline	0.6
Silane treated Si_3N_4	400

Paste B 11-3	Part by weight
Bis-GMA	80
TEGDMA	20
Benzoyl peroxide	0.8
Silane treated Si_3N_4	400

Paste A 11-4	Part by weight
Bis-GMA	80
TEGDMA	20
N,N-bis-(2-hydroxyethyl)-4-methylaniline	0.6
Silane treated α-SiO_2	400

Paste B 11-4	Part by weight
Bis-GMA	80
TEGDMA	20
Benzoyl peroxide	0.8
Silane treated α-SiO_2	400

Compressive strength, abrasion loss, toothbrush abrasion loss, amount of water sorption, linear thermal expansion coefficient, Knoop hardness, tensile strength, coloring property and bonding strength were measured of these various cured composite resins. Results were tabulated in Table 11(1) and Table 11(2).

Table 11(1)

	Monomer composition	Filler		Compressive strength (kg/cm^2)	Abrasion loss (cm^3)	Toothbrush abrasion loss (wt %)	Amount of water sorption (mg/cm^2)	Linear thermal expansion coefficient ($\times 10^{-6}/^{\circ}C$)
		Kind	Amount (wt%)					
1	TMM-3A(55)/TMM-4A(45)	Si_3N_4	80	3,200	0.19	0.054	0.30	20.5
2	"	α-SiO_2	"	2,780	0.40	0.100	0.28	26.5
3	Bis-GMA(80)/TEG(20)	Si_3N_4	"	2,530	0.31	0.120	0.42	26.1
4*	"	α-SiO_2	"	2,260	0.60	0.215	0.42	30.0

* indicates Control.

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Table 11(2)

	Monomer composition	Filler		Knoop hardness	Tensile strength (kg/cm^2)	Coloring property (ΔE)		Bonding strength (kg/cm^2)		
		Kind	Amount (wt %)			Fosished	Un-polished	Bovine enamel		Bovine dentin
								(1)	(2)	
1	TMM-3A(55)/ TMM-4A(45)	Si_3N_4	80	81	490	2.68	4.73	60-70	-	10-15
2	"	α-SiO_2	"	70	470	2.21	4.92	60-70	100-105	10-15
3	Bis-GMA(80)/TEG(20)	Si_3N_4	"	74	410	2.35	4.90	30-40	-	0-5
4*	"	α-SiO_2	"	54	360	3.88	10.23	30-40	-	0-5

* indicates Control.

It follows from the above table that the composite resins belonging to the present invention (Run Nos. 1 - 3), as compared to the composite resin (Run No. 4) prepared by combining together the conventionally known composite resin-forming monomer and filler, have such characteristic features as to be less in the linear thermal expansion coefficient as well as in the amount of water sorption, toothbrush abrasion loss and discoloration or the like, besides markedly excellent mechanical strengths, such as compressive strength, abrasion resistance, Knoop hardness, tensile strength and so on, and markedly excellent bonding to the hard tissue of the human body, and can be advantageously used as medical or dental material. These excellent properties of the composite resins of the present invention are particularly marked in the composite resin (Run No. 1) with a combination of the monomer of the present invention and the filler of the present invention and these composite resins are enough applicable to molars requiring markedly high mechanical strengths.

In column of bonding to the bovine enamel in the above table, (1) indicates bonding strength when applying the composite resin as such to the bovine enamel and (2) bonding strength when coating the bovine enamel surface with a mixture of equal amounts of bonding agents A and B of following compositions found anew by the instant inventors and set forth in another co-pending Patent Application filed claiming the priority based on Japanese Patent Application No. 54-44751, followed by application of the composite resin. It is noted from a comparison of bonding strengths to the bovine enamel in (1) and (2) of Run No. 2 that it is very effective in the point of bondability if the composite resin is applied after precoating the hard tissue of the human body with the said bonding agent.

Bonding agent A	Part by weight
TMM-3A	98
Tetraisopropyltitanate	2
N,N-bis-(2-hydroxyethyl)-4-methylaniline	2

Bonding agent B	Part by weight
TMM-3A	98
Tetraisopropyltitanate	2
Benzoyl peroxide	2
2,5-di-tert. butyl-4-methylphenol	0.15

Example 12:

Paste A 11-1 and Paste B 11-1 and Paste A 11-2 and Paste B 11-2 mentioned in Example 11 were mixed respectively in equal amounts for the preparation of composite resins of Run Nos. 1 and 2 in the following Table 12. By using them cytotoxicity tests by tissue culture were conducted.

The composite resin was enclosed in a glass tube with a surface area of 28.3 mm^2, the specimen immediately after curing was immersed in 5 ml of culture medium (199) and rotated at a rate of 200 r.p.m. at 37°C for 24 hours and then 1 ml of the medium was interacted with L-cells (2.8×10^4) to count cell numbers after 2 days and after 4 days. Results were shown in Table 12.

Likewise, cytotoxity tests were conducted on the composite resin comprising Paste A 1-2 and Paste B 1-2 of Example 1 and results were also tabulated in Table 12.

Table 12

	Monomer composition	Filler		Cell numbers in 1 ml	
		Kind	Amount (wt %)	After 2 days	After 4 days
Blank	-	-	-	4.6×10^4	56×10^4
1	TMM-3A(55)/TMM-4A(45)	Si_3N_4	80	3.0×10^4	24×10^4
2	"	α-SiO_2	"	3.2×10^4	22×10^4
3*	Bis-GMA(80)/TEGDMA(20)	α-SiO_2	75	2.3×10^4	19×10^4

* indicates Control.

As clear from the above table, the composite resin of the present invention is less in the action of inhibiting the cell multiplication as compared to the conventional type of composite resin.

Example 13:

Clinical observations were conducted by the following procedure.

Caries of a patient was removed by a dental drill and it was cleansed with water and the enamel of the caries was immediately coated by a brush with 40% phasphate etching solution. After one minute it was cleansed with water and further dried in an air stream for the formation of a clean enamel surface.

Then, the enamel surface in the cavity including this surface was thinly coated by sponge cotton with a mixture of equal amounts of bonding agents A and B mentioned in Example 11. Respectively different composite resins were applied to the caries in molars and in anterior teeth. That is, the composite resin prepared by mixing Paste A 11-1 and Paste B 11-1 mentioned in Example 11 with powdered Si_3N_4 incorporated as the filler was applied to molars, whereas the composite resin prepared by mixing Paste A 11-2 and Paste B 11-2 mentioned in Example 11 with powdered α-SiO_2 incorporated as the filler was applied to anterior teeth. The composite resin prepared by mixing and kneading together these Paste A and Paste B in equal amounts was immediately enclosed in the cavity and simultaneously, the filled portion was pressed and held on with celluloid strips for 5 minutes whereby the composite resin was cured. After it was cured, the celluloid strips were removed, the form was put in order by the dental drill and treatment was finished.

The following are results of these clinical observations.

(1) Results of application to molars:

Class 1 and Class 2 cavities in molars, in particular were filled. There were 106 clinical cases.

Conventionally molars were being filled with dental amalgam restoratives, such as an amalgam of silver alloy and mercury. Various problems, however, were indicated of these dental amalgam restorative materials, such as lacking bonding strength with the tooth, low in the marginary seal, toxicity and so on.

The composite resin of the present invention is nearly freed of any such defects as seen in the dental amalgam restorative material. That is, it has sufficient bonding strength to the tooth and is free from fractures in filled marginary portions frequently occurring in the amalgam restorative material and hence, hardly any incidence of recurrent caries is observed.

The composite resin of the present invention had sufficient bonding force to the tooth and it was freed from the fracture in the filled marginary portion frequently occurring at the time of filling with the dental amalgam and incidence of recurrent caries arising therefrom was hardly observed. Further, the composite resin of the present invention has excellent mechanical strengths, such as compressive strength, abrasion resistance, tensile strength and so on, in addition to steadfast bonding to the tooth and because of this, it hardly fell out even if enclosed in molars being more high in the occlusal pressure than anterior teeth.

It follows from these clinical test results that the composite resin with a combination of the composite resin-forming monomer belonging to the present invention and the metal nitride powdery filler of the present invention can fully withstand the practical use even if applied to molars and is superior in the performances to the widely used dental amalgam restoratives as the conventional molar restorative filling material.

(2) Results of application to anterior teeth:

Class 3 and Class 5 cavities, in particular, were filled. There were 129 clinical cases. Conventionally anterior teeth were being filled with dental composite

resins. These existing dental composite resins, however, are weak in mechanical strengths, such as compressive strength, abrasion resistance and so on, and low in bonding strength and hence, indications were made of various problems, such as incidence of recurrent caries on the contact surface between the restorative filling material and the tooth with the lapse of time after the filling, discoloration and surface abrasion arising from biting, brush polishing and so forth.

The composite resin of the present invention, even with the lapse of sic (6) months' time after its filling, was almost free from such problems as indicated o of the existing dental composite resin. The composite resin of the present invention was set free from recurrent caries in the interface with the tooth because of the resin having high bonding strength to the tooth and high abrasion resistance. Not only that, but hardly any discoloration was observed.

These results of clinical observations show that the composite resin comprising a combination of the composite resin-forming monomer belonging to the present invention and the existing metal oxide powdery filler should be markedly excellent in the performances when applying as the anterior tooth restorative filling material as compared to the existing dental composite resin.

CLAIMS:

1. A composition of restorative material, especially useful as a dental filling material, comprising finely divided inorganic filler material and polymerizable monomer components, characterized by:

(A) from about 50 to about 95 % by weight of finely divided, inorganic filler material which is safe and effective for use in a dental filling in the human body, wherein at least 50 % by weight of said filler material is at least one nitride substance having a Moh's hardness of at least 7 and is selected from the group consisting of vanadium nitride, boron nitride, aluminum nitride, silicon nitride, titanium nitride and zirconium nitride, and

(B) from about 50 to about 5 % by weight of polymerizable monomer component capable of polymerizing to form a binder resin for dental filling materials.

2. A composition according to claim 1, characterized in that said nitride substance is vanadium nitride, boron nitride, aluminum nitride or silicon nitride.

3. A composition according to claim 1 or claim 2, characterized in that said nitride substance has a particle diameter of 50 microns or less.

4. A composition according to claim 1 or claim 2, characterized in that said nitride substance has a Moh's hardness of at least 9.

5. A composition according to claim 1 or claim 2, characterized in that said nitride substance is coated with a silicon-containing keying agent.

6. A composition according to claim 5, characterized in that said silicon-containing keying agent is a silicon-containing organic compound having at least three alkoxy groups.

7. A composition according to claim 5, characterized in that said silicon-containing keying

agent is a silicon-containing organic compound having three alkoxy groups and one organic group possessing, as a terminal group, a mono-olefinic hydrocarbon radical, a primary amino group or an epoxy group.

8. A composition according to claim 5, characterized in that said silicon-containing keying agent is α-methacryloxypropyl-trimethoxysilane or vinyltriethoxysilane.

9. A composition according to claim 1, characterized in that the nitride is in powder form.

10. A composition according to claim 1, characterized in that nitride of metal other than the said metals is present.

11. A composition according to claim 1, characterized by the form of two pastes, one paste consisting essentially of a mixture of said nitride substance, said polymerizable monomer (B), and an activator for activating polymerization of (B), and the second paste consists essentially of a mixture of said inorganic dental filler substance different from said nitride substance, said polymerizable monomer (B) and a catalyst for catalyzing polymerization of (B).

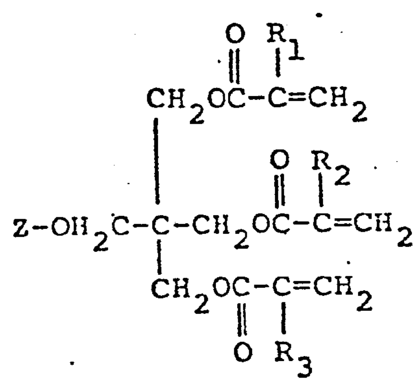
12. A composition of restorative material, especially useful as a dental filling material, comprising a mixture of polymerizable monomers of the acrylate or methacrylate type respectively and inorganic particulate filler characterized by

(A) from about 50 to about 95 % by weight of

finely divided, inorganic filler material and which is safe and effective for use in a dental filling in the human body, wherein at least 50 % by weight of said filler material is at least one nitride substance having a Moh's hardness of at least 7 and is selected from the group consisting of vanadium nitride, boron nitride, aluminum nitride, silicon nitride, titanium nitride and zirconium nitride, and the balance of said filler material is one or more inorganic dental filler substances which are different from said nitride substance, have a Moh's hardness of at least 5 and are useful as a filler for dental filling materials, and

(B) from about 50 to about 5 % by weight of polymerizable monomer component capable of polymerizing to form a binder resin, wherein said monomer component consists essentially of

(i) from 60 to 100% by weight of at least one, first polymerizable monomer having the formula (I)



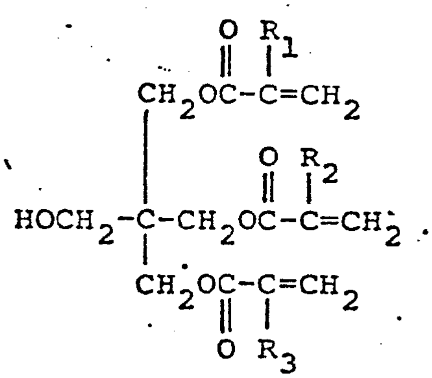
wherein Z is hydrogen or $CH_2{=}\overset{R_4}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-$, and R_1, R_2, R_3

and R_4, which are the same or different, each is selected from the group consisting of hydrogen, methyl, ethyl or n- or iso-propyl, and

(2) up to 40 % by weight of at least one, second polymerizable monomer which is different from said first polymerizable monomer and is suitable for use as a resin-forming monomer for dental filling materials.

13. A composition according to claim 12, characterized in that said filler material has a particle diameter of 50 microns or less.

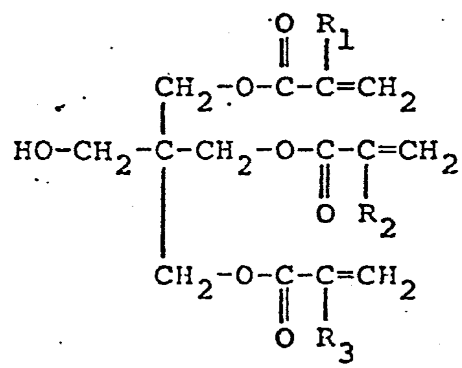
14. A composition according to claim 12, characterized in that said first monomer comprises at least one compound having the formula (II):



wherein R_1, R_2 and R_3 have the same meanings as defined in the formula (I).

15. A composition according to claim 12, characterized in that said first monomer consists essentially of

(1) 30 to 100 % by weight of at least one compound having the formula (II):

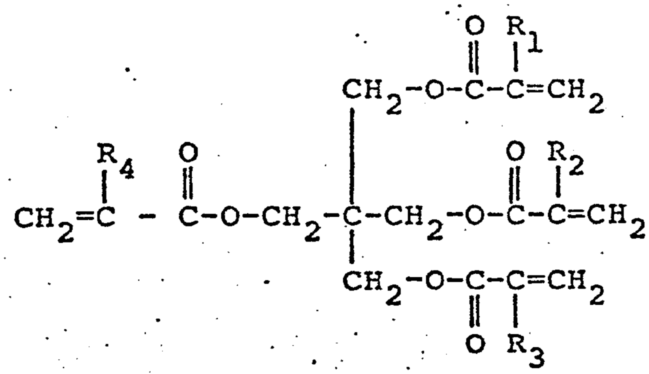


wherein R_1, R_2 and R_3 have the same meanings as defined in the formula (I)

and

(2) 0 to 70 % by weight of at least one compound

having the formula (III):



wherein R_1, R_2, R_3 and R_4 have the same meanings as defined in the formula (I).

16. A composition according to claim 12, characterized in that said first monomer consists essentially of 45 to 70 % by weight of at least one compound having the formula (II) and 30 to 55 % by weight of at least one compound having the formula (III).

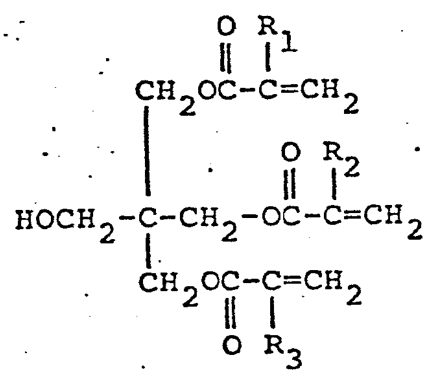
17. A composition according to any of preceding claims 12 to 15, especially useful as a dental filling material, characterized by:

(A) from about 70 to about 90 % by weight of finely divided, inorganic filler material having a particle size in the range of 0.1 to 50 microns and which is safe and effective for use in a dental filling in the human body, wherein at least 50 % by weight of said filler material is at least one nitride substance having a Moh's hardness of at least 7 and is selected from the

group consisting of vanadium nitride, boron nitride, aluminum nitride, silicon nitride, titanium nitride and zirconium nitride, and the balance of said filler material is one or more inorganic dental filler substances, which are different from said nitride substances, have a Moh's hardness of at least 5 and are useful as a filler for dental filling materials, and

(B) from about 30 to about 10 % by weight of polymerizable monomer component capable of polymerizing to form a binder resin for dental filling materials, said polymerizable monomer component consisting essentially of

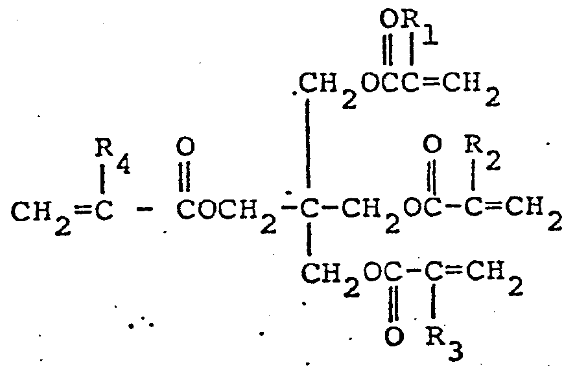
(1) from 40 to 80 % by weight of at least one, first polymerizable monomer having the formula (II)



wherein R_1, R_2 and R_3, which are the same or different, are hydrogen or methyl, ethyl or n- or iso-propyl

(2) from 20 to 60 % by weight of at least one

second polymerizable monomer having the formula (III)



wherein R_1, R_2, R_3 and R_4, which are the same or different, are hydrogen or methyl.

18. A composition as claimed in claim 17, characterized in that said filler material consists essentially of said nitride substance.

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EUROPEAN SEARCH REPORT

0092260
Application number

EP 83 10 3965

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
Y	US-A-3 991 008 (TEMIN et al.) * Column 1, lines 5-11; column 3, line 14 - column 5, line 28; column 6, line 33 - column 7, line 10; claims 1-16 * ---	1-18	A 61 K 6/08 A 61 F 1/00
Y	US-A-3 632 677 (PETNER et al.) * Column 1, lines 39-45; column 9, lines 5-11; claims 1-5 * ---	1-18	
Y	US-A-3 930 076 (KLIMENT) * Column 2, lines 41-60; column 4, line 58 - column 5, line 17; example 3; claims 3,14 * ---	1-18	
Y	GB-A-1 356 445 (KABUSHIKI KAISHA TOYOTA CHUO KENKYUSHO) * Claims 4,5 * ---	1-18	**TECHNICAL FIELDS SEARCHED (Int. Cl. 3)**
Y	GB-A-1 463 948 (SULZER BROTHERS LTD.) * Page 1, lines 36-46, 60-74; page 1, line 87 - page 2, line 3 * ---	1-18	A 61 K A 61 L
Y	US-A-3 261 800 (COLLINS III) * Column 1, lines 1-4, 47-55; column 2, example 4 * --- -/-	1-18	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16-08-1983	BENZ K.F.

CATEGORY OF CITED DOCUMENTS

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
A	CHEMICAL ABSTRACTS, vol. 88, no. 20, 15th May 1978, pages 334,335, no. 141644s, Columbus, Ohio, USA G. TSCHULENA et al.: "Some properties of insulating protective films on oxidized silicon in a biological environment" & PROC. INT. VAC. CONGR., 7th 1977, 3, 2035-2037 * Abstract * ---	1-18	
A	FR-A-2 400 354 (FRIEDRICHSFELD) * Claims 1-3 * ---	1-18	
A	GB-A-1 446 709 (NATIONAL PATENT DEVELOPMENT CORP.) * Claims 1-12 * -----	1-18	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)

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